

A Study of Electrochemical Reduction of Ethylene and Propylene Carbonate Electrolytes on Graphite Using ATR-FTIR Spectroscopy

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It is well known that when propylene carbonate (PC) is used as the primary solvent with common inorganic salts like LiPF_6 there is essentially continuous electrolyte reduction with a graphite electrode at ca. 0.9 V vs. Li/Li^+ , accompanied by gassing and graphite exfoliation¹⁻³. However, co-intercalation and subsequent reduction occurs only with PC and not the chemically closely related solvent ethylene carbonate (EC) or the other non-cyclic esters of carbonic acid, e.g. dimethyl carbonate (DMC), diethyl carbonate (DEC) or methyl ethyl carbonate (EMC). In the present work, we present results testing the hypothesis that there is a different reaction pathway for the electrochemical reduction of PC versus EC at graphite electrodes. We examined the reduction products formed on commonly used particulate graphite material using ex-situ Fourier Transform Infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode.^{4,5}

The graphite anodes laminated on the 25 μm thick copper current collector were composed of 92% MAG-10 graphite (Sumitomo) and 8 wt% PVDF (Kureha) with a loading of 3.64 mg/cm^2 . Electrochemical cells were assembled in Ar filled glove box (water and oxygen contents < 10 ppm.). The electrochemical cell were of the Swagelok® type assembled using the graphite anodes (1 cm^2 area), Li reference and counter electrodes, and a Celgard (3501) separator. The electrolytes used were 1.2M LiPF_6 /ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 wt%) (Quallion) and 1.0M LiPF_6 /Propylene Carbonate (PC) (Molicell). The graphite anodes were galvanostatically charged/discharged at a low rate of C/25 (50 $\mu\text{A}/\text{cm}^2$). Prior to FTIR spectral analysis, the discharge procedure (lithium deintercalation) was applied to avoid further Li-electrolyte reaction during rinsing and spectroscopic analysis.

The charging curve for the MAG-10 anode in PC based electrolyte had the expected profile shown in the insert to Fig. 1. The electrode clearly could not be intercalated with Li in this electrolyte, with the potential remaining at ca. 0.9 V vs. Li/Li^+ . The resulting spectrum A, shown in Fig. 1 for the rinsed sample, was remarkably different from that of any sample from the EC-based electrolyte. The spectrum could be easily resolved into two molecular components as shown by the companion spectra from reference compounds, lithium carbonate (Li_2CO_3) (spectrum B) and lithium methoxide (CH_3OLi) (spectrum C). In contrast, the spectrum (Fig. 2A) from anode formed in EC based electrolyte is substantially different, both qualitatively and quantitatively, from that of PC. The passivation film formed on the graphite anode in EC:EMC/ LiPF_6 is composed (in descending order of concentration) of compounds chemically similar to lithium oxalate, lithium methoxide, polyethers like PEO or poly-THF, and lithium carbonate.

The results clearly show there is a different pathway for reduction of PC versus EC on graphite electrodes, the one with PC leading nearly entirely to lithium carbonate as the solid product (and presumably

ethylene gas as the co-product) while EC follows a path producing products having a uniquely different components, e.g. poly-oxyethylene and lithium oxalate. Possible differences in reaction pathways will be discussed.

References

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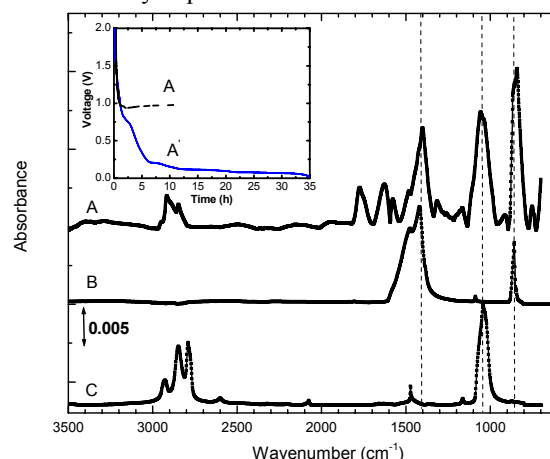


Figure 1. FTIR spectra of (A) SEI layer formed on graphite anode after potential reached plateau at ca. 0.9 V vs. Li/Li^+ in 1M LiPF_6 /PC; (B) lithium carbonate (Li_2CO_3) and (C) lithium methoxide (LiOCH_3). Inset: First galvanostatic charging curve in graphite at C/25 using 1M LiPF_6 /PC (A) and 1.2 M LiPF_6 /EC:EMC (3:7) (A').

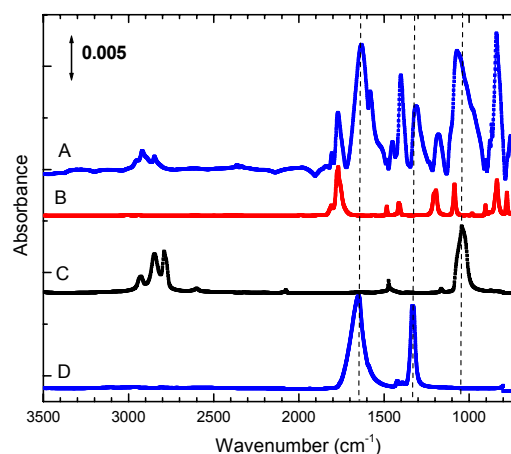


Figure 2. Spectrum (A) from graphite anode charged (Li intercalation) to 20 mV vs. Li/Li^+ and reference compounds: (B) EC- LiPF_6 precipitate; (C) lithium methoxide (LiOCH_3) and (D) lithium oxalate ($\text{Li}_2\text{C}_2\text{O}_4$).